Anisotropy and Magnetostriction of Some Ferrites

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Magnetic crystal anisotropy and magnetostriction have been measured in various single crystals of ferrites having compositions represented approximately by MFe_2O_4, where M stands for Mn, Fe, Co, Ni, and Zn in various proportions. Special attention is given to heat-treatment in a magnetic field.

The magnetic anisotropy of cobalt ferrite at room temperature is as high as 4×10^6 ergs/cm^3. Magnetostriction is as high as 800×10^{-6}. Magnetic anneal is effective at temperatures as low as 150°C, and causes the hysteresis loop to become square. In polycrystalline material the response to magnetic anneal is a maximum at compositions intermediate between $CoFe_2O_4$ and Fe_3O_4.

The constants for the various specimens are tabulated. Values of the anisotropy constants of $MnFe_2O_4$ at 20°C and −196°C are the same as those determined from ferromagnetic resonance experiments. At −196°C the constant for $Ni_{0.75}Fe_{2.25}O_4$ differs markedly from that determined by ferromagnetic resonance; this is to be expected from the relaxation phenomena observed by Galt, Yager, and Merritt.

IT is well known that some magnetic materials respond to heat treatment in a magnetic field: after cooling from an elevated temperature in the presence of a magnetic field, the domains are found to have a preferred direction parallel to the field, and the magnetic properties are correspondingly anisotropic. The chemically combined mixed oxides of cobalt and iron (cobalt ferrites) have been known to be responsive to such a heat treatment since the work of Kato and Takei.[1]

In an attempt to discover the explanation of this phenomenon, and to study the behavior of ferrites in other ways, experiments have been made on the crystal anisotropy and magnetostriction of several cobalt ferrites in both single-crystal and polycrystal forms. Special attention is given to the effect of heat-treatment. Measurements of these properties have also been made on a variety of other ferrites.

SPECIMENS

Most of the single-crystal specimens, grown by the flame fusion method, were obtained from Dr. G. W. Clark of Linde Air Products Company. Others were grown by J. P. Remeika of the Bell Laboratories; this work will be published shortly. The former crystals contained an excess of Fe_3O_4 over the formula $CoFe_2O_4$, the latter were nearly stoichiometric.

Most of the experiments on the effect of magnetic anneal on the crystal anisotropy were carried out on crystals of cobalt zinc ferrite, $Co_{0.32}Zn_{0.24}Fe_{2.18}O_4$. This formula and others given below are based on chemical analysis of the crystals measured for metallic elements, the remainder being assumed to be oxygen. If we assume the ions to be Zn^{++}, Co^{+++}, and Fe^{+++}, this can be written $(ZnO)_{0.22}\cdot(Co_2O_3)_{0.14}\cdot(Fe_2O_3)$; valences cannot be satisfied with Co^{++} instead of Co^{+++}. Single crystals of $Co_{0.78}Fe_{2.27}O_4$ were also examined; these correspond to $(CoO)_{0.78}\cdot(FeO)_{0.37}\cdot(Fe_2O_3)_{0.95}$. Continued heating in air at temperatures up to 600°C did not change the weights of the specimens.

Most of the polycrystalline specimens were prepared under the direction of J. W. Nielsen and were fired at 1200°C to 1250°C in an atmosphere of O_2 or CO_2. They were intended to cover the range of solid solutions extending from $CoFe_2O_4$ to Fe_3O_4.

The composition of these and other materials are given in Tables I and II.

CRYSTAL ANISOTROPY

Measurements of the torque in a saturating magnetic field were made on single crystal disks weighing less than 0.1 g, by using well-known techniques.[2] Figure 1 shows torque curves for a single crystal disk of cobalt zinc ferrite cut parallel to a (100) crystal plane, θ being the angle between the saturating field (or saturation magnetization, M_s) and the [001] crystal direction. When the specimen is heated at 150°C for three days with no magnetic field present ($H_T=0$) we obtain curve A, which shows the expected symmetry for a cubic crystal,

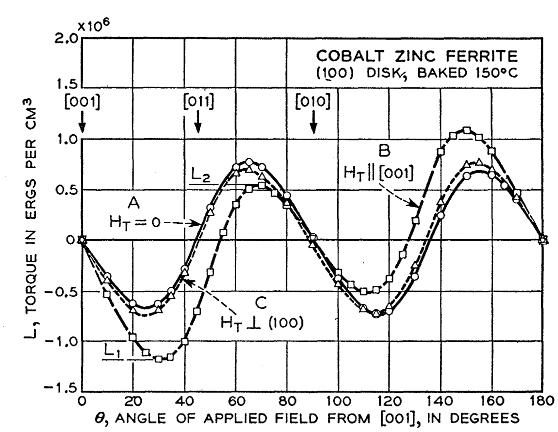

FIG. 1. Torque curves, showing the effect of magnetic anneal parallel and perpendicular to the (100) plane of measurement.

[1] Y. Kato and T. Takei, J. Inst. Elec. Engrs. (Japan) 53, 408 (1933).

[2] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), p. 556.

with easy directions parallel to the cubic axes. The torque is given closely by the theoretical relation $L=-\frac{1}{2}K_1 \sin 4\theta$, with the crystal anisotropy constant equal to $K_1=+1.5\times 10^6$ ergs/cm³.

After maintaining the specimen for the same temperature and time in the presence of strong magnetic field ($H_T=9000$ oersteds) parallel to [001], curve B is obtained. This shows that the stability of the easy direction parallel to H_T has been enhanced, while that of the easy direction at right angles to H_T, [010], has been diminished. The difference in the crystal anisotropy energy between the [001] and [010] directions is now 0.5×10^6 ergs/cm³, whereas it was formerly zero.

When the specimen is annealed with $H_T\perp$ (100) plane, it is noted that the torque measured in this plane is practically the same (curve C) as when no field was present during annealing (curve A).

Measurements of the torque on a disk cut parallel to a (110) plane of the same crystal are shown in Fig. 2 for

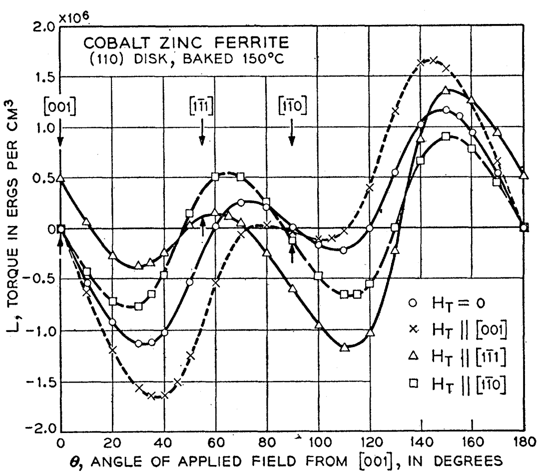

Fig. 2. Effect of magnetic anneal in various directions in the (110) plane.

various directions of H_T. The effect of the direction of the field present during heat treatment is clearly shown. Here we find not only differences in the relative energies, depending on the direction of H_T, but also a shift in the directions of easy magnetization. These occur at $L=0$, when $dL/d\theta<0$, and are parallel to the [001] and [11̄0] directions when $H_T=0$.

The results given above can be described by the superposition of an uniaxial anisotropy on the normal cubic anisotropy. The whole crystal anisotropy can then be expressed as follows:

$$E=K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2)+K_T\sin^2(\theta-\theta_T), \quad (1)$$

the α's being the direction cosines of the saturation magnetization, M_s, with respect to the crystal axes, θ_T the angle between H_T and the nearest crystal axis, and θ the angle between M_s and [001]. The torque is then

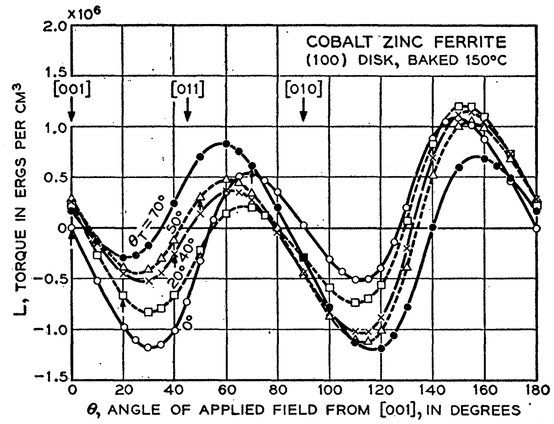

Fig. 3. Effect of magnetic anneal in various directions in the (100) plane, θ_T being angle between [001] direction and direction of field during anneal.

$L=-dE/d\theta$, and for the (100) plane is

$$L=-\tfrac{1}{2}K_1\sin 4\theta-K_T\sin 2(\theta-\theta_T), \quad (2)$$

when H_T lies in the plane.

To test this relation further, measurements were made with the (100) disk with H_T varied in approximately 10° steps from [001] to [010] in (100). The resulting torque curves (Fig. 3) were analyzed by evaluating the components containing $\sin 2\theta$, $\cos 2\theta$, $\sin 4\theta$, and $\cos 4\theta$. The measured torque curves (Fig. 3) were found to be composed of terms proportional to $\sin 2\theta$, $\cos 2\theta$, $\sin 4\theta$, and $\cos 4\theta$, with no appreciable residual. Accordingly, the curves were analyzed into these components,[3] the calculations being facilitated by the use of a punched card machine. Writing the expression for L in the form

$$L=a_2\sin 2\theta+a_4\sin 4\theta+b_2\cos 2\theta+b_4\cos 4\theta, \quad (3)$$

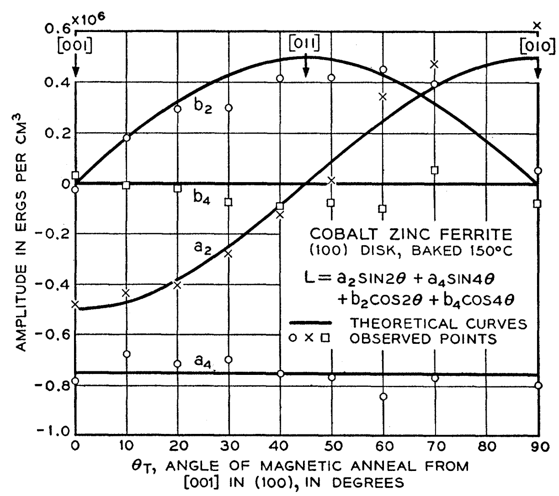

Fig. 4. Amplitudes of 2θ and 4θ components of torque curves [see Eq. (3)].

[3] This was done with the kind cooperation of Dr. R. W. Hamming and Miss F. Maier.

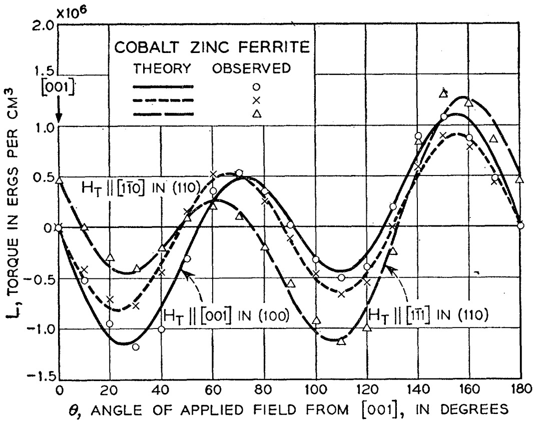

FIG. 5. Observed points, and lines calculated for three principal cases, using constants $K_1=1.5\times10^6$, $K_T=0.5\times10^6$.

and comparing with the previous expression for L, we have

$$a_2=-K_T\cos2\theta_T,\quad a_4=-K_1/2,\quad b_2=K_T\sin2\theta_T,\quad b_4=0.$$

The values of a_2 to b_4, derived by analysis of the torque curves, are plotted in Fig. 4 as points and there they can be compared with the expected values shown by the lines drawn for $K_1=1.5\times10^6$, $K_T=0.5\times10^6$ ergs/cm³.

It will be noted in Fig. 3 that the direction of easy magnetization may depart from the cubic axis by somewhat more than 10°. Larger departures are noted in Fig. 5; here points show measurements made on the (100) and (110) specimens and the curves are calculated from Eq. (1) using the above chosen values of K_1 and K_T. Theoretical and observed directions of easy magnetization for the (100) disk are plotted in Fig. 6 as lines and points, respectively.

To test for any possible variation of K_T with θ_T, K_T was derived from each curve of Fig. 3 and plotted against θ_T (see Fig. 19). No trend is observed.

It follows from the above described behavior of the single crystals that a polycrystalline material should respond to magnetic anneal in a degree determined by K_T alone. Material was prepared by L. G. Van Uitert to correspond in composition to the single crystal of cobalt zinc ferrite. After heat treatment in a magnetic field at 150°C, the torque curve of the polycrystalline material was found to have an amplitude of 0.54×10^6 ergs/cm³, close to the chosen value of $K_T=0.5\times10^6$.

The changes in the torque curves of cobalt zinc ferrite with magnetic anneal may be contrasted with the changes produced[4] in magnetite by cooling through its transformation temperature at about −140°C. In the latter material the direction of easy magnetization remained very close to a crystal axis when the strong field applied during cooling through the transformation temperature was 30° or less from the axis, and departed widely from an axis when the field was near 45°. This change of the direction of easy magnetization with the direction of the field present during cooling is shown for magnetite in Fig. 6, curve E, where it can be compared with the data for cobalt zinc ferrite, curve A. The different behavior of the two materials suggests that different mechanisms are operating.

Two other estimates have been made of the anisotropy of cobalt ferrite. Weisz[5] has derived the absolute value of K_1 from measurements of the initial permability, μ_0, of polycrystalline material, using the relation

$$\mu_0-1=21M_s^2/K_1.$$

This assumes that the change in magnetization takes place by a rotational process alone, and assumes a partly empirical constant of proportionality. His value of $|K_1|=3.5\times10^6$ compares with our measured value of $K_1=1.8\times10^6$, for the material nearest stoichiometry. Constants for other stoichiometric simple ferrites are given in his original paper. In the case of stoichiometric $NiFe_2O_4$ Weisz's estimated value of $|K_1|=400\,000$ is to be compared with $K_1=62\,000$ determined by Galt, Matthias and Remeika.[6]

Shenker[7] has measured K for cobalt and nickel ferrites by observing the torque in a measured field which is insufficient to saturate. Results are reported for temperatures of 20 to 800°K. The method is based essentially on the known relations

$$L=-HM_s\sin(\theta_0-\theta)=-\tfrac{1}{2}K_1\sin4\theta,$$

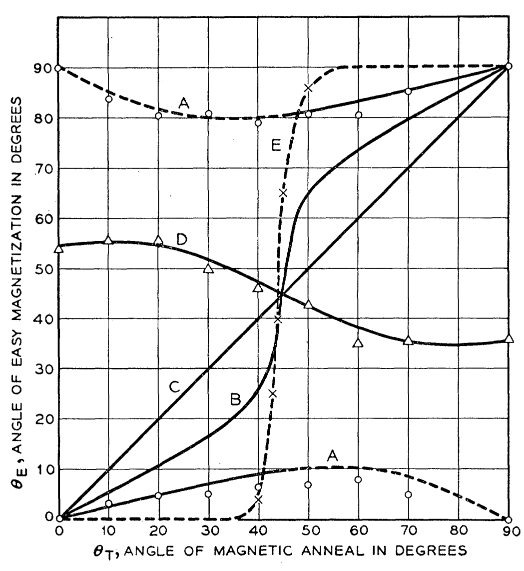

FIG. 6. Dependence of direction of easy magnetization on the direction in which the field was applied during heat treatment in the (100) plane. Points, observations. Lines are: (A) for chosen values $K_T/K=0.5/1.5=\frac{1}{3}$, (B) for $K_T/K=1$, (C) for $K_T/K=\infty$. Theoretical and observed directions of hard magnetization are shown by (D). Data for Fe_3O_4 are represented by broken line (E), to show the difference in type of curves. In (A), solid lines show easiest directions, dotted lines, secondary easy directions.

[4] Williams, Bozorth, and Goertz, J. Appl. Phys. **91**, 1107 (1953).

[5] R. S. Weisz, Phys. Rev. **96**, 800 (1954).

[6] Galt, Matthias, and Remeika, Phys. Rev. **79**, 391 (1950).

[7] H. Shenker, thesis, University of Maryland, 1955 (unpublished); and private communication.

θ and θ_0 being the respective angles that M_s and H make with [001] in the (100) plane. When θ_0 is small, L can be plotted against $1/H$ and extrapolated to $1/H=0$. This gives the torque for infinite field, which is $-2K\theta_0$, and so K_1 is evaluated. M_s may also be obtained from the slope of the curve used for extrapolation.

A more exact method is to plot a series of curves for $2/\sin 4\theta$ *vs* $\sin(\theta_0-\theta)$, for various values of θ_0. Then for given θ_0 one measures $-L/HM_s$ [equal to $\sin(\theta_0-\theta)$] and reads off $-K/L$ (equal to $2/\sin 4\theta$) from the appropriate curve, and then obtains K_1 from the measured value of L. This assumes that M_s is known.

Shenker's values of K for a crystal of composition $Co_{1.12}Fe_{2.21}O_4$ are 3.8×10^6 for 20°C and 17.5×10^6 for -196°C. The former may be compared (Table I) with our values for specimens of different compositions. Shenker's values of K_1 for $Ni_{0.47}Co_{0.05}Fe_{1.39}O_4$ for these temperatures are also given in this table ($K_1=-42\,900$ and $-27\,800$, respectively).

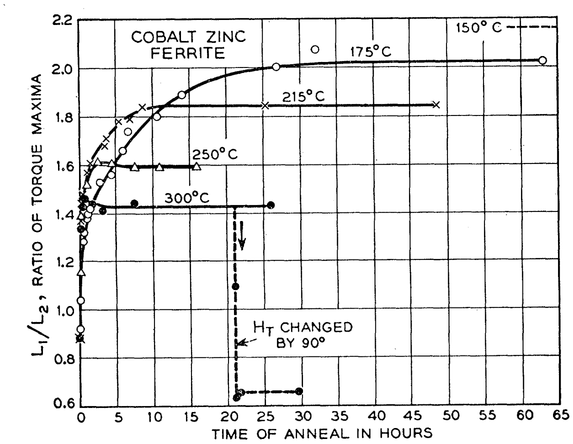

FIG. 7. Anisotropy as dependent on time of magnetic anneal. L_1 and L_2 as designated in Fig. 1, curve B. Dotted curve shows effect of changing direction of magnetic anneal by 90 degrees, from [001] to [010].

TEMPERATURE AND TIME EFFECTS

The measurements described above were made after the specimen had been held at 150°C for three days. The magnitude of the effect is dependent on both the temperature and time of treatment in a field, as well as on the magnitude of the field. As a measure of the effect we used the ratio of the first minimum to the first maximum of the torque curves, designated as in Fig. 1 as L_1 and L_2. This ratio is plotted in Fig. 7. The change of L_1/L_2 with time of treatment shows that a change is taking place, to which a relaxation time may be assigned. Plotting the logarithm of this relaxation time against the reciprocal of the absolute temperature, as shown in Fig. 8, one obtains the activation energy of 0.94 ev.

It is apparent from Fig. 7 that a different limiting value of L_1/L_2 is approached for each temperature of magnetic anneal. The limiting values are plotted against

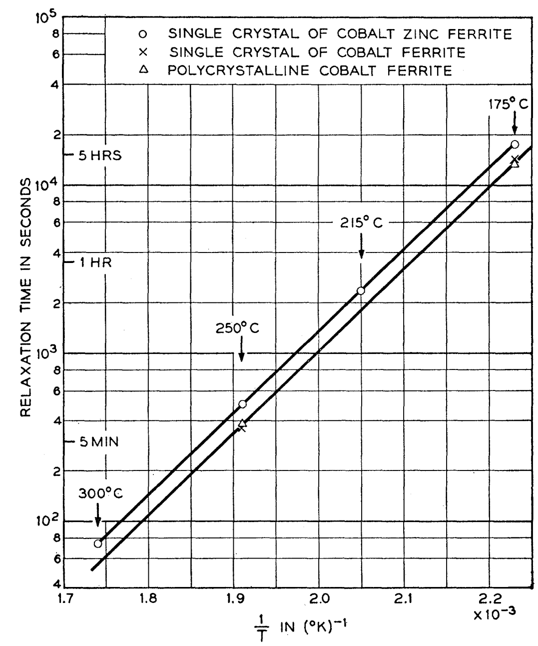

FIG. 8. Relaxation time of effect of magnetic anneal for (a) cobalt ferrite single crystal, (b) cobalt zinc ferrite single crystal, (c) cobalt ferrite polycrystal. Activation energy, 0.94 ev.

temperature in Fig. 9. The ratio is higher the lower the temperature of anneal, and drops in an almost linear fashion to one at the Curie point.

The same specimen, a disk with dimensional ratio 2.36, was used to determine the strength of the field necessary for effecting a magnetic anneal. The data of Fig. 10 show that an applied field of 500 oersteds will cause about half of the maximum change in L_1/L_2. Since this is about half of the demagnetizing field for saturation magnetization, the field inside the material (applied field minus demagnetizing field) is presumably much smaller. This is confirmed by measurements on a hollow square specimen as described below.

OTHER FERRITES

The single crystal of cobalt ferrite of composition $Co_{0.78}Fe_{2.27}O_4$ was used in some experiments like those

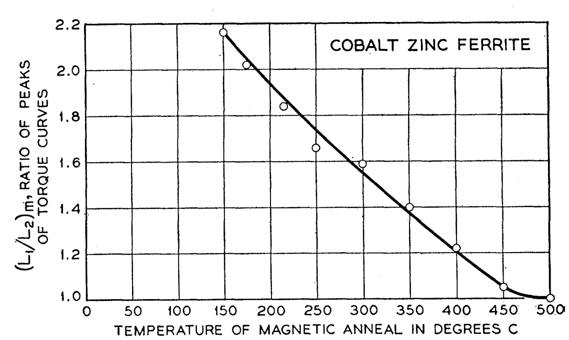

FIG. 9. Effect of magnetic anneal at various temperatures, measured by the ratio of the two peaks of the torque curves in the (100) plane.

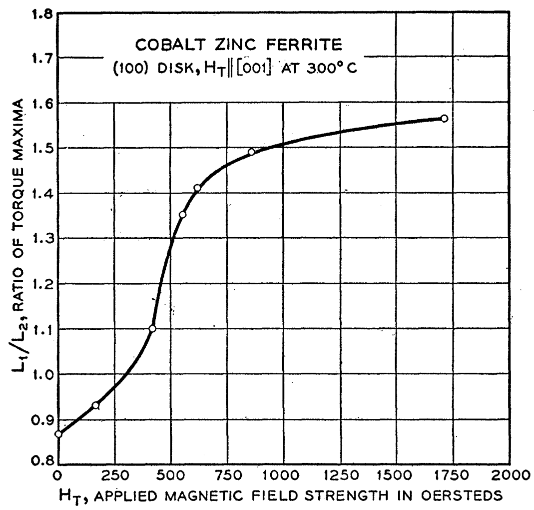

FIG. 10. Effect of strength of field, H_T, present during annealing of (100) disk, on the magnetic anisotropy as measured by the ratio of the maxima in the torque curve.

performed on cobalt zinc ferrite. A torque curve for a (100) disk, heated at 150°C with $H_T \| [001]$, is shown by the solid line in Fig. 11. Before analyzing into its 2θ and 4θ components this curve had to be corrected[8] for lack of saturation even in a field strength of 25 000 oersteds. The corrected points are shown as triangles, and the accompanying dotted curve is the best line through them that contains only sines and cosines of 2θ and 4θ. The analysis gives $K_1 = 4.3 \times 10^6$, $K_T = 2.5 \times 10^6$ ergs/cm^3, values considerably higher than those for cobalt zinc ferrite. The curve obtained after treatment in zero field was somewhat irregular in shape, showing definite lack of saturation and possibly other disturbing effects. Therefore K_1 was deduced from the curve for $H_T \| [001]$, as mentioned above.

The cobalt ferrite of composition $Co_{1.1}Fe_{1.9}O_4$, nearly stoichiometric, was found to have the much lower crystal anisotropy constant of $K_1 = 1.8 \times 10^6$. It did not respond to magnetic anneal, therefore $K_T = 0$.

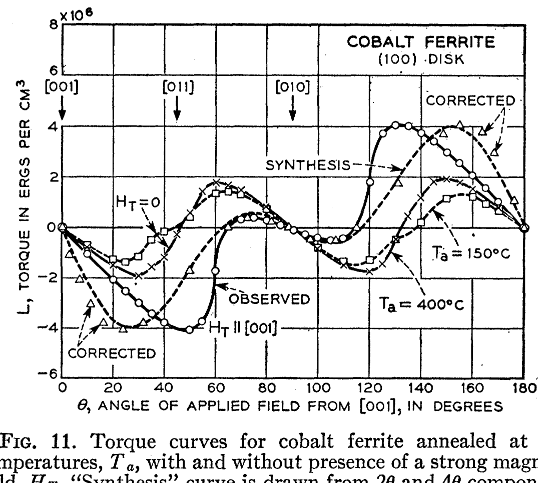

FIG. 11. Torque curves for cobalt ferrite annealed at two temperatures, T_a, with and without presence of a strong magnetic field, H_T. "Synthesis" curve is drawn from 2θ and 4θ components derived originally from corrected points (triangles).

[8] As proposed by H. J. Williams. See Bozorth, Phys. Rev. **96**, 311 (1954).

Some other ferrites, of manganese, nickel, and manganese-zinc, were examined and the results are given in Table I.[4,7,9–15] Direct comparison was made with the results on manganese ferrites obtained at microwave frequencies.[9] Pieces for both kinds of experiments were cut from the same ferrite crystal. It is noted that the results are the same for the two methods, well within the experimental error.

The results for nickel ferrite at room temperature may be compared with the previous data obtained by Galt and collaborators[16,17] and by Healy.[11] Some differences are apparent. Not enough data are available to determine quantitatively the effect of small differences in chemical composition.

TABLE I. Crystal anisotropy constants of some ferrites.

Composition	K_1 at 20°C	K_1 at −196°C	Reference
Fe_3O_4	-1.1×10^3	···	12
Fe_3O_4	-1.35×10^3	···	4
[b] { $Co_{0.8}Fe_{2.2}O_4$	3.9×10^6 [a]		
{ $Co_{0.8}Fe_{2.2}O_4$	2.9×10^6 [c]	4.4×10^6	
$Co_{1.1}Fe_{1.9}O_4$	1.8×10^6		
$Co_{1.1}Fe_{2.2}O_4$	3.8×10^6	17.5×10^6	7
$Co_{0.3}Zn_{0.2}Fe_{2.2}O_4$	1.5×10^6		
$Co_{0.3}Mn_{0.4}Fe_{2.0}O_4$	1.1×10^6		
$Mn_{0.45}Zn_{0.55}Fe_{2.0}O_4$	-3.8×10^3		13
$MnFeO_4$	-28×10^3	-187×10^3	
[b] { $Mn_{0.98}Fe_{1.86}O_4$	-34×10^3	-240×10^3	
{ $Mn_{0.98}Fe_{1.86}O_4$	-33×10^3 [d]	-233×10^3 [d]	9
[b] { $Ni_{0.8}Fe_{2.2}O_4$	-39×10^3	-42×10^3	
{ $Ni_{0.8}Fe_{2.2}O_4$	-43×10^3 [d]	-74×10^3 [d]	10
$Ni_{0.75}Fe_{2.25}O_4$	-49×10^3 [d]		14
$Ni_{1.0}Fe_{2.0}O_4$	-63×10^6 [d]	-87×10^3 [d]	15
$NiFe_2O_4$	-51×10^3 [d]	$+20\times10^3$ [d]	11
$Ni_{0.7}Co_{0.002}Fe_{2.2}O_4$	-18×10^3	-125×10^3	
$Ni_{0.7}Co_{0.004}Fe_{2.2}O_4$	-10×10^3	-196×10^3	
$Ni_{0.47}Co_{0.05}Fe_{1.4}O_4$	-43×10^3	-28×10^3	7

[a] Quenched in air from 400°C.
[b] Brackets indicate that measurements were made on different specimens cut from the same crystal.
[c] Aged at 150°C for 3 days.
[d] Constant derived from measurements at microwave frequencies. Others at zero frequency (torque method).

Bickford *et al.*[18] have shown that addition of only a small amount of cobalt ferrite to magnetite changes the sign of the anisotropy constant from negative to positive. Our experiments extend this idea to additions to nickel ferrite. The anisotropy constant of nickel ferrite is reduced from about −40 000 to −10 000 by the

[9] Private communication from S. Geschwind and J. F. Dillon.
[10] Private communication from Cetlin, Galt, Merritt, and Yager.
[11] D. W. Healy, Phys. Rev. **86**, 1009 (1952).
[12] L. R. Brickford, Phys. Rev. **78**, 449 (1950).
[13] Galt, Yager, Remeika, and Merritt, Phys. Rev. **81**, 470 (1951).
[14] Yager, Galt, and Merritt, Phys. Rev. **99**, 1203 (1955).
[15] Yager, Galt, Merritt, and Wood, Phys. Rev. **80**, 774 (1950).
[16] Galt, Yager, and Merritt, Phys. Rev. **93**, 1119 (1954).
[17] J. K. Galt, Bell System Tech. J. **33**, 1023 (1954).
[18] Bickford, Pappis, and Stull, Office of Naval Research Technical Report, January, 1954 (unpublished).

addition of only 0.4 mole percent of cobalt ferrite (attempted composition).

It is possible that the variable estimates of K_1 for nickel ferrite may be attributed to a slight variable impurity of cobalt.

Specimens cut from the same crystal of $Ni_{0.8}Fe_{2.2}O_4$ were used for microwave measurements by Cetlin, Galt, Merritt, and Yager, and for static measurements by the authors. Results show a decided difference between the K_1's determined at $-196°C$, and some difference also at room temperature. The large difference at $-196°C$ is in accord with the relaxation phenomena reported by Galt *et al.*[16,17] This is discussed in a recent note.[18a]

MAGNETOSTRICTION

Measurements of magnetostriction and of crystal anisotropy were made on the same crystals. Using the strain-gauge technique,[19] magnetostriction was determined usually in the [001] and [011] directions in the (100) plane, as dependent on field strength up to 25 000 oersteds, the field being applied parallel or perpendicular to the gauge. Specimens were heat-treated in various ways, with or without the presence of a strong field during the heat treatment. Some of the materials showed an unusually large magnetostriction.

One can determine from the magnetostriction data the distribution of domains resulting from a given heat treatment.

Results are shown in Fig. 12 for $Co_{0.3}Zn_{0.2}Fe_{2.2}O_4$, the specimen having been treated (a) in zero field ($H_T=0$)

TABLE II. Magnetostriction constants of some ferrites. Also saturation magneostriction, $\bar{\lambda}$, of polycrystalline material, calculated from these constants. Values are for room temperature unless noted.

Composition	$\lambda_{100}\times 10^6$	$\lambda_{111}\times 10^6$	$\bar{\lambda}\times 10$
Fe_3O_4[19]	−19	81	41
Fe_3O_4(124°K)[16]	−23	55	24
$Co_{1.1}Fe_{1.9}O_4$	−250	—	—
$Co_{0.8}Fe_{2.2}O_4$	−590	120	−210
$Co_{0.3}Zn_{0.2}Fe_{2.2}O_4$	−210	110	−18
$Co_{0.3}Mn_{0.4}Fe_{2.0}O_4$	−200	65	−40
$Ni_{0.8}Fe_{2.2}O_4$	−36	−4	−17
$Mn_{0.98}Fe_{1.86}O_4$	−35	−1	−15
$Mn_{0.6}Zn_{0.1}Fe_{2.1}O_4$	−14	14	3

and (b) in a high field parallel to [001]. For this and other substances examined the results are interpreted in terms of the coefficients λ_{100} and λ_{111} which appear in the well-known expression[20] for the magnetostriction $\lambda=\Delta l/l$ in a cubic crystal:

$$\lambda=(3/2)\lambda_{100}(\alpha_1^2\beta_1^2+\alpha_2^2\beta_2^2+\alpha_3^2\beta_3^2-1/3)+3\lambda_{111}(\alpha_1\alpha_2\beta_1\beta_2+\alpha_2\alpha_3\beta_2\beta_3+\alpha_3\alpha_1\beta_3\beta_1).$$

[18a] Bozorth, Cetlin, Galt, Merritt, and Yager, Phys. Rev. **99**, 1898 (1955).
[19] J. E. Goldman, Phys. Rev. **72**, 529 (1947).
[20] See reference 2, p. 650.

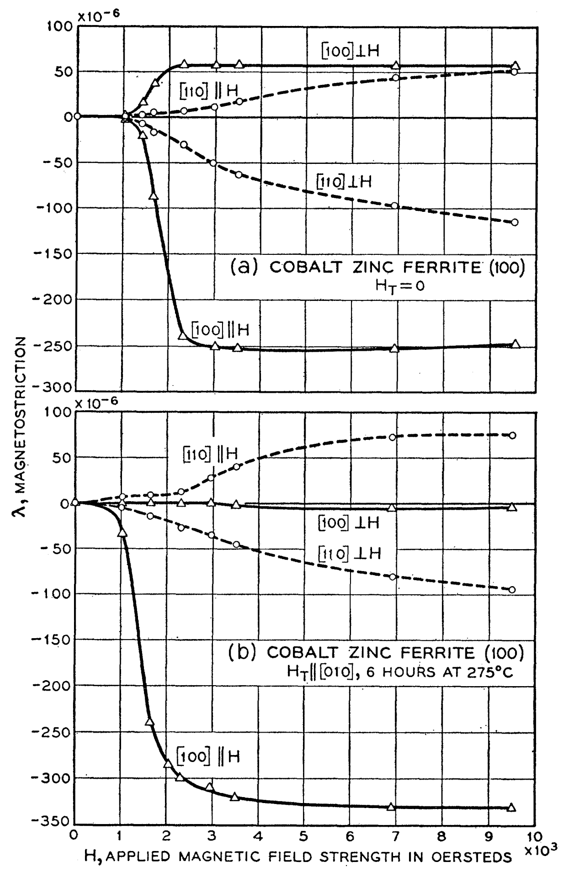

FIG. 12. Magnetostriction in Co-Zn-ferrite after treatment in (a) zero field, and (b) strong field parallel to [010] in (100) plane.

Here the α's are the direction cosines of the saturation magnetization, and the β's those of the measured change in length, with respect to the crystal axes. In any given specimen, with given distribution of domains in the initial (demagnetized) state, the constants are evaluated by magnetizing to saturation first in one direction, then in another, and noting the difference. In most of the experiments reported here, λ_{100} was determined by placing a gauge parallel to [001] in (100) and measuring the change in length when the material was saturated in the plane in directions first parallel and then perpendicular to the gauge. Then $\lambda_{100}=\lambda_{\parallel}-\lambda_{\perp}$ in [001]; similarly, using a gauge placed parallel to [011] in (100), $\lambda_{111}=\lambda_{\parallel}-\lambda_{\perp}$.

The same values of λ_{100} and λ_{111} were derived from the data of (a) and (b) of Fig. 12, and these are given in Table II. In (a), for which $H_T=0$, it is apparent that the domains were initially distributed almost equally among the 6 directions of easy magnetization, [001], $\cdots$. In (b), for which $H_T\|[001]$, the domains were initially aligned parallel and antiparallel to [001], where they were fixed by the magnetic anneal. It should be noted that the magnetostriction in this direction is zero; therefore, essentially all of the domains were oriented

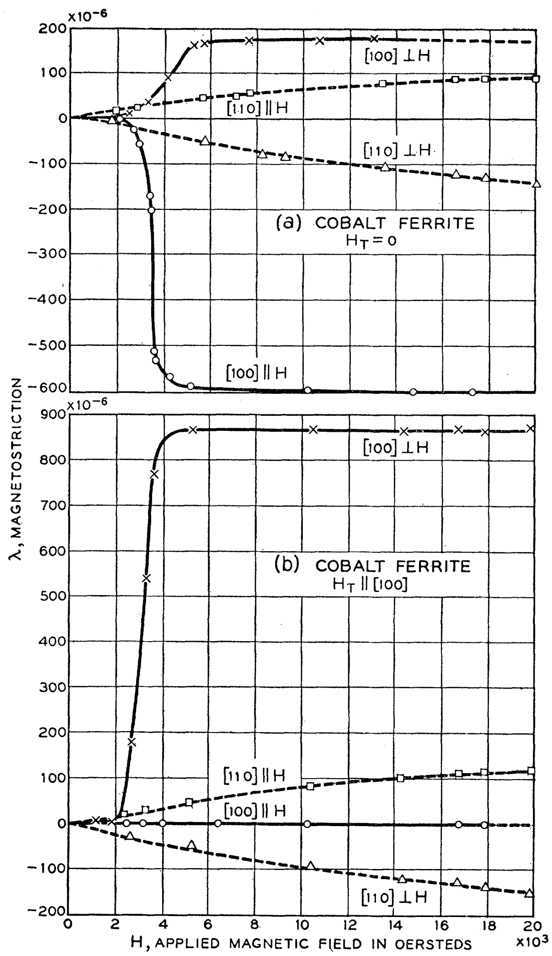

FIG. 13. Magnetostriction of cobalt ferrite crystal (a) without and (b) with magnetic anneal. Derived constants in Table II.

originally parallel to [001], although a shallow minimum in the crystal anisotropy energy occurs also ||[010], a subsidiary direction of easy magnetization as shown by the torque curve B of Fig. 2.

Similar data for $Co_{0.8}Fe_{2.2}O_4$ are shown in Figs. 13 (a) and (b), and the derived values of λ_{100} and λ_{111} are the same for the two sets (see Table II). The initial domain distribution is fixed, as for cobalt zinc ferrite, by the magnetic anneal (direction of H_T), when this is parallel to a crystal axis.

For this material the magnetostriction measured with the field and gauge perpendicular to H_T is very large, namely 740×10^{-6}. Measurements of this were repeated with a second specimen comprised of a rod of dimensional ratio length/thickness = 2.2 instead of with a disk. See Fig. 14. It was noted that the λ *vs* H curve is strictly reversible, even on the steep portion, the same points A and B being obtained on increasing as on decreasing H. The slope on the steep portion is equal to $d\lambda/dH = 0.5\times 10^{-6}$, and would presumably be much higher if the demagnetizing field of the rod (about 1000 oersteds at saturation) were smaller.

The smallness of the initial slope of the λ *vs* H curve is apparently associated with the high anisotropy of the specimen. The corresponding curve for the specimen heat-treated in zero field has a larger initial slope because in this material 90° domain walls can move so as to permit the magnetization to change from one direction of easy magnetization to another equally easy. When H_T is applied parallel to one crystal axis, the difference in the crystal anisotropy energy along the axis and one at right angles is $K_T = 2\times 10^6$ ergs/cm³.

The magnetostriction constants of single crystals of these and some other ferrites are given in Table II. The saturation magnetostriction of polycrystalline ferrites of these compositions are included in the table, as calculated from the relation $\bar{\lambda} = (2\lambda_{100} + 3\lambda_{111})/5$.

HYSTERESIS LOOPS

Since materials that respond to magnetic anneal often have square hysteresis loops, a specimen was cut from a single crystal in the form of a hollow square so that it could be measured with closed magnetic circuit. The length of the edges, cut parallel to [100] directions, was 3.7 mm, the thickness 1.2 mm, and the width of each leg 1.1 mm. Hysteresis loops for different fields present during annealing for 15 minutes at 400°C are shown in Fig. 15. Although sharp corners were not observed on the loops, remanence was considerably increased by magnetic anneal and the maximum effect was obtained when the field present during anneal, H_T, was about 10 oersteds. The coercive force was then about 5 oersteds. The lack of sharp corners may be due to the geometrical imperfection of the specimen. Unfortunately, the speci-

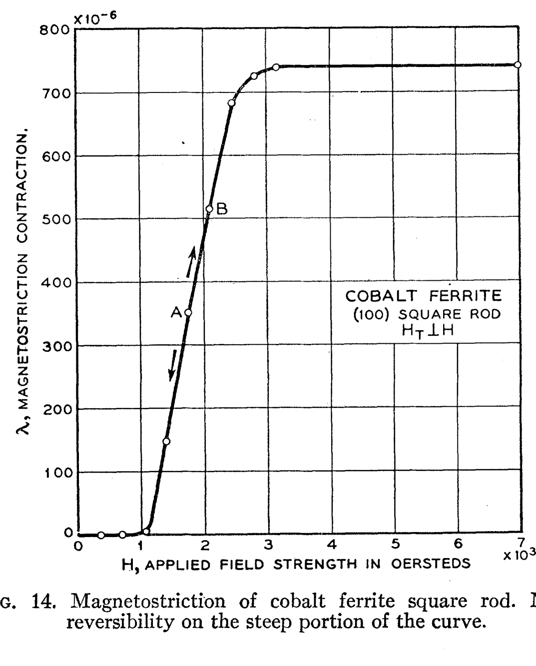

FIG. 14. Magnetostriction of cobalt ferrite square rod. Note reversibility on the steep portion of the curve.

men was broken before it could be annealed at right angles to its plane.

Powder patterns were made from portions of the specimen by Mr. R. C. Sherwood, after careful polishing and etching. These show the expected domain structure with parallel and antiparallel domains, the domain walls being always parallel to the edges of the magnetization and to the specimen. Figure 16 shows two of the patterns for the demagnetized state.

POLYCRYSTALLINE SPECIMENS

The experiments on single crystals of cobalt ferrite showed that the response of the material to magnetic anneal varied with composition. This response could be investigated most easily with polycrystalline specimens, and was determined for several compositions lying between $CoFe_2O_4$ and Fe_3O_4. Specimens were fired at 1250°C in O_2 or CO_2, depending on composition. The magnetic anisotropy created by the magnetic anneal, expressed as maximum torque per unit volume and given in Fig. 17, shows the already known lack of response at the two extremes and a rather high maximum in the middle. The highest measured anisotropy corresponds to $K_T = 2\times10^6$ ergs/cm^3.

The composition for maximum effect of heat treatment is consistent with the optimum composition of material used for permanent magnets, known as "O.P." or "Vectolite."

Ordinarily the magnetostriction of a material at saturation is considered to be a structure-insensitive property. In view of the change in some of the properties of ferrites with state of oxidation, it was suggested by L. G. Van Uitert that the dependence of saturation

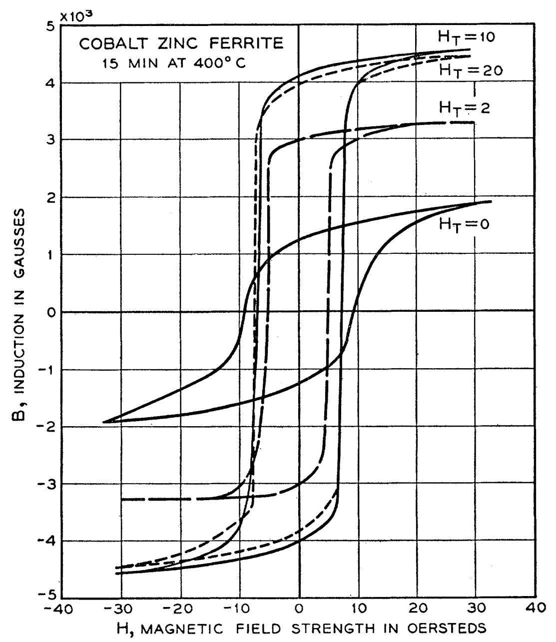

FIG. 15. Hysteresis loops of cobalt zinc ferrite showing effect of magnitude of field present during anneal, H_T, in oersteds.

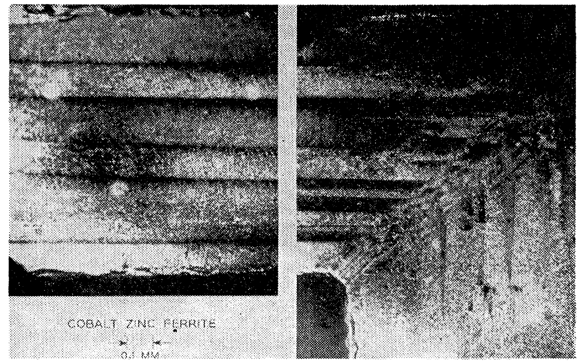

FIG. 16. Powder pattern on hollow rectangle of cobalt zinc ferrite, showing effect of magnetic anneal on domain orientation.

magnetostriction on state of oxidation be tested. Two polycrystalline specimens of nickel ferrite were selected from the same lot of material, having Fe/Ni = 1.87, and fired under different conditions of oxidation so that the ratio of their electrical resistivities was greater than 1000. Figure 18 shows the longitudinal and transverse magnetostrictions to be the same, within experimental error.

DISCUSSION

Anisotropy

Cobalt ferrite is characterized by high-positive crystal anisotropy, by a high-negative magnetostriction, and by response to magnetic anneal. All of these characteristics are at a maximum when some iron ferrite (magnetite) is present in solid solution, and they tend to lower values (and zero response to magnetic anneal) as the composition approaches stoichiometric $CoFe_2O_4$ or Fe_3O_4.

Addition of a small amount of cobalt ferrite to other ferrites is often enough to change their inherent negative anisotropy (easy direction, [111]) to positive,[21] and to make them respond to magnetic anneal. Addition of about 1 percent of $CoFe_2O_4$ to iron-rich $NiFe_2O_4$ seems to be enough to make the negative anisotropy of the latter decrease in magnitude and pass through zero to become positive.

Since the magnetostriction is large there is some possibility that it will contribute substantially to the anisotropy. The contribution has been expressed by Becker and Döring[22] as an additional anisotropy constant, ΔK_1:

$$K_1 = K_0 + \Delta K_1 = K_0 + (9/4)[\lambda_{100}(C_{11} - C_{12}) - \lambda_{111}C_{44}],$$

K_0 being the intrinsic crystal anisotropy constant, K_1 the observed constant, and ΔK the difference which is dependent on the magnetostriction and elastic constants. Calculation of $\Delta K_1/K_1$ for cobalt zinc ferrite, using the elastic constants determined by McSkimin

[21] J. L. Stull and L. R. Bickford, Phys. Rev. **92**, 845 (1953).
[22] R. Becker and W. Döring, *Ferromagnetismus* (Verlag Julius Springer, Berlin, 1939), p. 145.

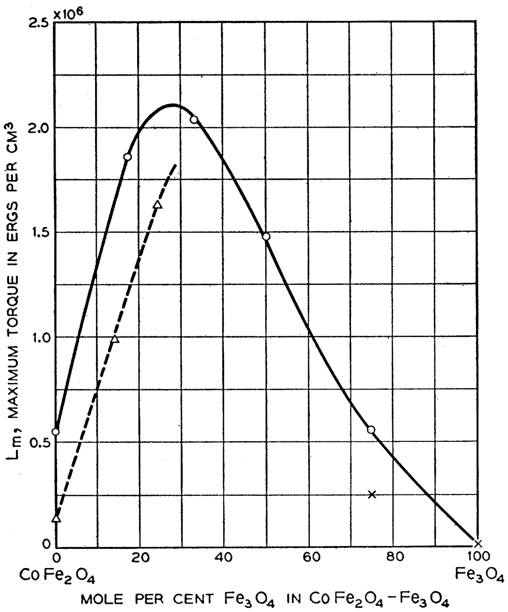

FIG. 17. Dependence of anisotropy, developed in polycrystal line material by heat treatment, on composition. Maximum torque, L_m, is equal to $K_T/2$. Attempted compositions; circles, fired in oxygen; crosses, fired in CO_2; triangles, another series fired in air.

and others,[23] is found to be only $70\times10^3/(1.5\times10^6)$ or less than 5 percent. Thus the contribution of magnetostriction to the anisotropy is small.

In the crystal of cobalt zinc ferrite the response to magnetic anneal was such as to make the selected direction an axis of easier magnetization, the difference in the energy between this direction and the direction at right angles being 0.5×10^6 ergs/cm^3. In iron-rich cobalt ferrite the response is similar in kind, but larger.

The origin of this difference in energy is so far not clear. The firmness by which the domains are held in the easy direction by the magnetic anneal, measured by K_T, can be compared with the elastic energy that is absorbed during the change of magnetization from one easy direction to another. Consider a crystal that has been heat-treated with the field parallel to [100], so that all domains are parallel to this axis, and then magnetize it to saturation parallel to another axis, [010]. The elastic energy so expended is $\lambda^2 Y$, where $\lambda=\frac{3}{2}\lambda_{100}$ and Y represents Young's modulus, and is

$$E=(9/4)\lambda_{100}(c_{11}-c_{12})(c_{11}+2c_{12})/(c_{11}+c_{12}).$$

This is 150 000 ergs/cm^3, which is to be compared with 500 000 ergs/cm^3, the difference in energy as determined from the torque curve. The domains are obviously held to the direction of easy magnetization by forces much stronger than those of magnetostriction.

Néel[24] has proposed a theory of short range order and its effect on the magnetostriction and crystal anisotropy. In relation to the present experiments it suggests that the short range order is controlled by the magnetic anneal and that as a result there will be a uniaxial anisotropy superposed on the normal crystal anisotropy. The magnitude of the uniaxial anisotropy, however, should be dependent on the crystallographic direction according to Néel's theory, and in a face-centered cubic lattice the constant K_T should be twice as large when $H_T\|[110]$ as it is when $H_T\|[100]$. In our experiments no such crystallographic dependence was observed. In order to check on this point our torque curves were analyzed and K_T, the amplitude of the 2θ component, was derived separately from each curve for the (001) plane. The results, given in Fig. 19, show no trend that approaches the magnitude required by Néel's theory for a *simple* face-centered lattice. In a private communication Professor Néel has pointed out that the various interactions between neighbors, either between nearest-neighbors, second-nearest neighbors, or through super-exchange, is so complicated that it is uncertain if there should be any dependence of K_T on crystallographic direction in the ferrites. The results, then, are not necessarily in conflict with Néel's theory.

Note added in proof.—In an attempt to detect atomic ordering, E. Prince has made neutron diffraction observations on cobalt ferrites of various compositions, both before and after heat treatment in a magnetic field. The neutron data show no evidence of long range order of Fe and Co on octahedral sites, but the possibility of some short range order cannot be eliminated. The magnetic structures of heat-treated samples contain moments which are not in general aligned parallel to [100] directions, the angle of misalignment being greater in iron-rich samples in accordance with the magnetic observations. We are indebted to Dr. Prince for permission to include this note in our paper.

Chikazumi[25] measured the effect of magnetic anneal on the anisotropy of a crystal of composition $FeNi_3$, and found a uniaxial anisotropy, K_T, of magnitude 450 to

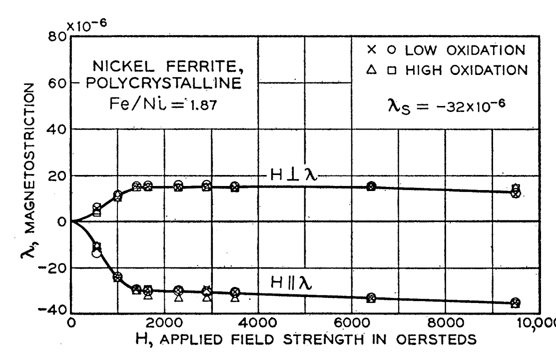

FIG. 18. Magnetostriction of polycrystalline nickel ferrite, showing negligible effect of oxidizing anneal which changed conductivity 1000-fold.

[23] Using the elastic constants determined on a piece of the same crystal by McSkimin, Williams, and Bozorth, Phys. Rev. **95**, 616 (1954).

[24] L. Néel, J. phys. radium [8] **15**, 225 (1954).

[25] S. Chikazumi, as reported by S. Kaya, Revs. Modern Phys. **25**, 49 (1953).

1250 ergs/cm³. In accordance with Néel's theory, and unlike our measurements on Co-Zn-ferrite, the uniaxial anisotropy of $FeNi_3$ depends on the crystallographic direction.

Another possible explanation to be considered in the explanation of our results is the formation of thin plates or rods of precipitate that are directed by the magnetic field during the anneal, in much the way that they are[26] in Fe_2NiAl and Alnico 5. According to calculation, the torque of a rod-like precipitate at saturation is

$$L=\tfrac{1}{2}(N_t-N_l)M_s^2\sin 2\theta,$$

N_l and N_t being the longitudinal and transverse demagnetizing factors of the rods. In cobalt zinc ferrite the amplitude of the 2θ term, 0.5×10^6, would be realized by a rod-like precipitate having $N_t-N_l\approx 2\pi$, corresponding to a large ratio of length/diameter. Plates having appropriate dimensional ratios might also satisfy the experimental data. The nonsinusoidal character of the torque curves of cobalt ferrite, seen in Fig. 11, supports the idea that a separate phase is precipitated at low temperatures and that its direction is controlled by the field during annealing.

The time constants used in determining the energy of activation, (Figs. 7 and 8), correspond to the expression for the relaxation time:

$$\tau=\tau_0 e^{w/kT},$$

the energy of activation being 0.94 ev. The magnitude is consistent with the time necessary for the diffusion of atoms in a solid of this kind. No specific data on the diffusion constants of any of the elements in these materials, or their temperature dependence, are known to us.

It is surprising at first to find the relaxation time of magnetic anneal, as shown in Fig. 7, to be so rapid at temperatures as low as 150°C. It should be remembered, however, that the ferrite structure is built up of a lattice of relatively large and deformable O^{--} ions with much smaller metal ions in the interstices. It is therefore reasonable to observe the effects of the diffusion of the relatively small metal atoms at this low a temperature; the diffusion of C and N in iron take place with comparable speeds at even lower temperatures. The relaxation time of cobalt ferrite reduces to about 1 second at the Curie point.

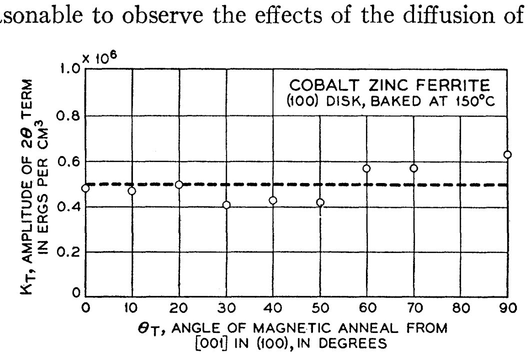

FIG. 19. Constants K_T derived from harmonic analysis of torque measured in (100) plane, for various angles θ_T between H and [001].

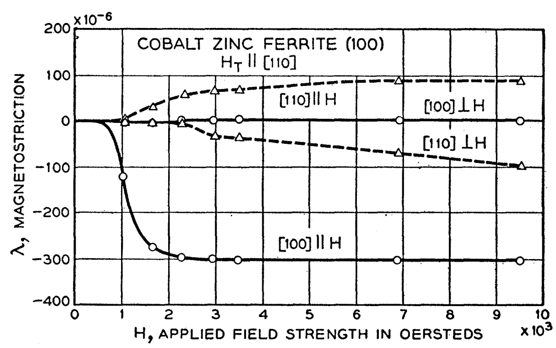

FIG. 20. Magnetostriction of Co–Zn-ferrite in (100) plane. See Table II for derived constants.

The temperatures required for the sintering of ferrite powder are hundreds of degrees higher than the temperatures at which magnetic anneal is effective. It is suggested that the diffusion of the O^{--} ions, which control the lattice structure, occurs with appreciable rapidity only at the higher temperatures needed for sintering, while the much greater mobility of the metal ions at the lower temperatures controls the magnetic properties.

It will be noted that τ_0 for the process under discussion is about 10^{-6} sec, a time long compared with 10^{-13} sec, the time of oscillation of an atom in the lattice. This means that many oscillations take place before an atom can escape from a potential well, or that it must escape successively from many wells before it finds a position where it causes a change in the property observed, in this case crystal anisotropy.

Magnetostriction

Composition.—Insufficient data are available to show uniquely the effect of composition on the magnetostriction constants. It is apparent, however, that the presence of Co causes a large negative value of λ_{100} and a moderately large positive λ_{111}. Apparently higher λ_{100}'s are obtained when there is somewhat less than one Co atom per molecule. The effect of the valence of the atoms (in nickel ferrite) has no apparent effect on magnetostriction.

Crystal symmetry.—In the ferrites examined $\lambda_{100}<0$, and generally $\lambda_{111}>0$. In most cases $|\lambda_{100}|>|\lambda_{111}|$, and in some cases $|\lambda_{100}|$ is very large. The high magnetostriction emphasizes the fact that crystals which are originally cubic have lower symmetry when magnetized. Guillaud and Sage[27] have even observed by x-rays the difference in spacing between (001) and (100) planes

[26] Nesbitt, Williams, and Bozorth, J. Appl. Phys. **25**, 1014 (1954).

[27] C. Guillaud and M. Sage, Compt. rend. **237**, 313 (1953). See also C. Guillaud, Revs. Modern Phys. **25**, 64 (1953).

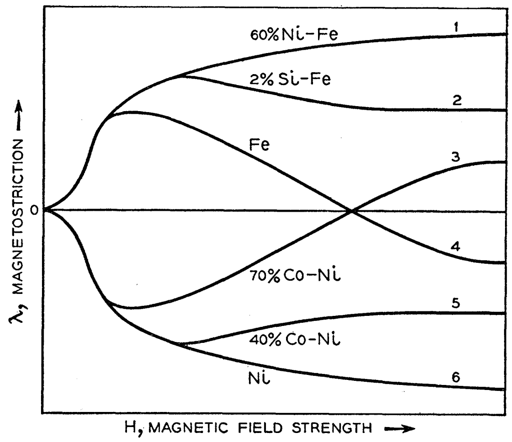

FIG. 21. Various types of magnetostriction curves expected from various relations between K, λ_{100} and λ_{111}. See Table III.

when the direction of magnetization is differently related to these planes.

This raises the question as to when to take account of the effect of the magnetostriction on the crystal symmetry. One point of view that we believe to be tenable is the following. When a crystal such as iron is unmagnetized and its spins are distributed equally among the six directions of easy magnetization, it is cubic, because the properties measured in various directions in a crystal of reasonable size have the required symmetry (four 3-fold symmetry axes). This is so even though the unit cell, and also a single domain, have only tetragonal symmetry, and these subdivisions of nickel have rhombohedral symmetry. If either of these crystals is magnetized along one axis it is tetragonal, and if magnetized in an arbitrary direction it is triclinic.

Initial domain distribution.—The magnetostriction at saturation is useful not only in determining the values of the constants λ_{100} and λ_{111} but also in deducing the domain distribution in the unmagnetized state. For example, Fig. 13 shows that when cobalt ferrite is magnetically annealed with $H_T \| [100]$, the longitudinal magnetostriction in this direction is zero, therefore in the unmagnetized state all of the domains are oriented either parallel or antiparallel to this direction. Even though [010] is also a direction of easy magnetization, practically all of the domains are fixed $\|[100]$.

After annealing the same specimen with $H_T \| [110]$ it was found (see Fig. 20) that practically all of the domains were aligned nearly parallel to [100] and none $\|[010]$. In this case [100] and [010] are equally easy and equally near to H_T, and one might expect half of the domains to be nearly parallel to each axis. Presumably H_T was slightly nearer to one axis than to the other and the nearer axis was chosen. It may be that a very slight error in adjusting the angle of H_T will result in the alignment of the domains almost parallel to one or the other of the axes. The torque curve for this treatment (see Fig. 6) shows the easy direction to lie about 10° from the crystal axes.

Form of λ, *H curve.*—Bickford, Pappis, and Stull[18] have studied the behavior of λ *vs* H curves of Fe_3O_4 and of solid solutions containing a few percent of $CoFe_2O_4$. They note that in Fe_3O_4 at room temperature the magnetostriction is positive at low values of H, and that it becomes negative when the temperature is lowered below 160°K and [100] becomes the direction of easy magnetization ($K_1 > 0$). As they point out, the initial part of the λ, H curve depends on the sign of λ in the easy direction, and the latter part of the curve shows the effect of the sign of λ in the hard direction.

This idea may be generalized, and the relation of the signs of K_1, λ_{100}, and λ_{111} to the general shape of the λ, H curve may be tabulated. It is convenient to distinguish

TABLE III. Types of magnetostriction curves (λ *vs* H). See Fig. 20.

K_1	λ_{100}	λ_{111}	Curve type	Examples
+	+	+	1	60% Ni−Fe
+	+	−	2, 4	2% Si−Fe, Fe
+	−	+	3, 5	
+	−	−	6	
−	+	+	1	
−	+	−	3, 5	70% Co−Ni, 40% Co−Ni
−	−	+	2, 4	
−	−	−	6	Ni

6 types of curves as indicated in Fig. 21, the type depending on the presence or absence of maxima or minima, and on the existence of a crossing of the curve through $\lambda = 0$. The situations that give each type of curve are given in Table III, and some materials that fall into various classes are noted.

ACKNOWLEDGMENTS

We are indebted to P. W. Anderson, C. Herring, H. J. Williams, E. A. Nesbitt, and J. K. Galt for valuable discussions on various phases of this work. We are also indebted to S. Millman for valuable comments on the manuscript, and to S. Geschwind and J. F. Dillon, to B. B. Cetlin, J. K. Galt, F. R. Merritt, and W. A. Yager, for permission to quote their values of K_1 obtained from microwave data before publication.

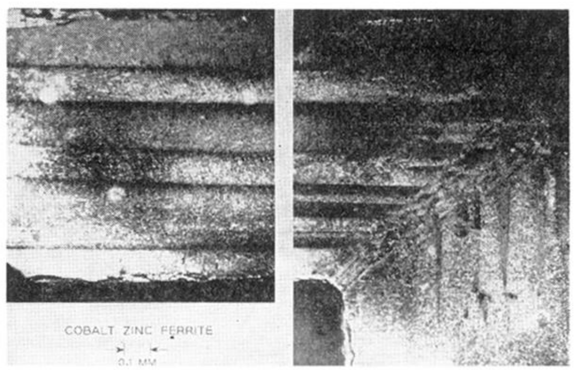

FIG. 16. Powder pattern on hollow rectangle of cobalt zinc ferrite, showing effect of magnetic anneal on domain orientation.